Keeping Water Quality of the River Ganga – Some Scientific Aspects

By

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Dedicated to..........

All My Well Wishers.............

Certificate

This is to certify that the work contained in the thesis titled: *Keeping Water Quality of the River Ganga – Some Scientific Aspects*, by *Mr Subhankar Basu* has been carried out under my supervision.

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Abstract

The genesis of the present research was the belief since ages and the observations made through some studies that the water of the river Ganga has unique characteristics which allows sustenance of quality on prolonged storage. Very few systematic studies have been conducted to support the contention that the Ganga water indeed has some special composition that could be attributed to its unique "keeping quality". The research work presented in this thesis was directed to address the issue of keeping quality of Ganga water. It was postulated that the keeping quality would depend on the ability to arrest microbial activity which is generally responsible for deterioration in water quality on prolonged storage. Hence attempts were made to collate information on water quality parameters that are likely to influence the microbial activity in unpolluted stretches of the river Ganga. For comparison, other three Indian rivers, viz. Yamuna, Godavari and Narmada were selected. Some field studies that involved collection and analysis of sediment and water samples of the four rivers in the vicinity of their respective origins were conducted. Emphasis was on estimation of heavy metals, radioactive elements, dissolved carbon and other physicochemical parameters such as temperature, pH, alkalinity, hardness and dissolved oxygen. Based on the available information regarding the impact of heavy metals, radioactive elements vis-à-vis the chemical composition of water on the microorganisms in the aquatic environment, an overall impact score for the waters of the four Indian rivers selected in the study has been assigned. The Ganga water gets the highest impact score for arresting microbial activity due to unique combination of heavy metal content and presence of radioactive elements associated with low hardness and low dissolved carbon content. The impact score is higher by an order of magnitude compared to the waters of the other three rivers. It appears that the grain size distribution of Ganga sediments play an important role in determining the water quality despite the observations that the sediments of other rivers may have same or slightly higher content of heavy metal and radioactive elements.

Keywords

Indian Rivers, River Ganga, River Yamuna, River Godavari, River Narmada, Water Quality, Keeping Water Quality, Heavy Metals, Sediments, Radioactive Elements, Radio Activity, Microbial Activity.

1. Prologue

The Ganga River is considered to be the holiest river in India with religious importance. It originates at Gaumukh from the icy glacial deposits of Gangotri as "Bhagirathi". It has been observed that the water quality of the river Ganga is such that no foul smell is produced even after prolonged storage in closed containers. This is contrary to the common observation that the quality of river water generally deteriorates on storage due to microbial activities. This special characteristic of river Ganga is considered to be very significant. It has been argued that taking up any storage or diversion projects on the river Ganga may adversely influence this special character. Government of India appointed a high level committee to look into this matter when such an issue came up while executing Tehri Dam project on river Bhagirati. The committee could not support the issue of special quality of Ganga water due to lack of scientific evidence/studies despite the several observations and general belief over ages.

Some literature reports associate the special keeping quality of water of the river Ganga to the presence of trace metals, radioactive elements and bacteriophages. The ability of extremely small amounts of most trace metals to exert a lethal effect upon microorganisms in the aquatic environment has been well established. Radioisotopes of U, Th, Ra and other heavy ions present in rocks and bed sediments in trace amounts goes into solution depending upon oxidation-reduction potential (ORP) and emit radiation. Alpha particles affect the cells because they give up their energy over a relatively short distance. Thus, alpha particles inflict more severe biological damage than other radiations.

Physico-Chemical influences on the toxicity and the uptake of trace metals to different fresh water aquatic microorganisms have been studied by several workers over the last few decades. It was found that variation in water temperature, pH, alkalinity, hardness DO, and dissolved organic compounds influence the uptake of metals.

While presence of trace metals and radioactive elements in Ganga water and their role in control of microbial growth is a plausible explanation for the keeping quality, such elements have also been reported in other river waters which do not exhibit such special

qualities. The present study therefore attempts to address the issue of the exceptional keeping water quality of the river Ganga through investigation of some scientific aspects related to the presence of trace metals and radioactive elements vis-à-vis the control of microbial activity in the aquatic environments. For comparison, three other Indian rivers, namely Yamuna, Godavari and Narmada have been included in this study.

2. Literature Review

2.1 Scope

Rivers occupy an important place in human civilization. It is a boon for living and developments. In India, rivers are considered to be sacred with religious importance. From the distant past Ganga River has occupied an important place in Hindu religion. The river is known for its holiness. People have found that this river's water has a unique 'keeping quality'. The river water does not deteriorate even after keeping for a long period. With increasing populations and urbanization along the banks of the river, it receives huge quantities of untreated industrial and domestic wastewater and solid wastes. However, it has been found that the Ganga River has an enormous capacity of purifying it and retains its virginity. Several studies by different workers have been done at different stretches of the river from Haridwar to Calcutta. However, very few studies have been reported on the higher and lesser Himalayan regions. Review of literature presented in this thesis collates the information on the quality of river waters not significantly influenced by anthropogenic activities i.e. in the stretches close to the origin of the rivers. Emphasis has been laid on geochemical and physicochemical aspects that may have an impact on river water quality from the point of view of control of microbial growth on prolonged storage.

2.2 General

The river Ganga occupies an unrivalled position among the rivers of the world. No other river is so closely identified with a country as the Ganga is with India. Nor has any river elsewhere in the world influenced to a greater extent the life of the country through which it flows (Mahajan, 1994). The Ganga River has been esteemed as beneficent, giver of health and prosperity and the purifier of sin. The word 'Ganga' is derived from the etymological root 'gam', meaning, "to go". Ganga is the "Swift-Goer" and the running; flowing and energetic movement of her waters is constantly mentioned as one of the major reasons behind her purifying attributes (Exotic India, 2004).

Foreign travelers were fascinated by the veneration in which the Ganga was held by the people at a large. They noted in particular the unique quality of its water, which they found

sweet, pleasant, wholesome and potable even when kept for a longer time. In the common history of the country this river was called Foshwui, the *river of religious merit.*

The Mughal Empire used to carry Ganga water while traveling because it was considered much lighter than the other waters (Joannes, 1631). Hamilton (1820) stated that the Ganga water was esteemed for its medicinal properties besides its sanctity. Withington (1968) reported that any worm or fleas do not breed within the Ganga water carried many hundred miles and kept for longer. Ashok (2001) through a review of historical documents noted that the Ganga water was of such high quality that it could be stored for years without decomposing. It was attributed to its holiness. But science provides a non-holy explanation. Waste matter in water gets neutralized by interaction with oxygen-the process is called oxygenation. The Ganga gets huge doses of oxygen from the air as it cascades down its upper reaches. In its lower reaches, its huge surface area enables it to imbibe much oxygen from the atmosphere. In this way the Ganga constantly purifies itself.

Mahajan (1994) examined the water of Ganga in Varanasi. The water was collected at the mouths of the sewers where it emptied into the river. The sewer water, containing *Cholera* germs, mixed with water from river Ganga was kept for six hours; and at the end of six hours all germs were dead. The process was repeated 2-3 times and the outcome was same every time. In a similar way repeatedly *Cholera* germs were put into pure well water, which was barren of any life. After six hours the number increased to millions.

2.3 Synoptic View of the Lithology of the Drainage Basins

The drainage area of the river Ganga in hills lies in the north central of the Kumaun Lesser Himalaya (Garhwal Himalaya). The geology of the area has been studied in great details by a number of workers (Gannser, 1964; Jain, 1971; Tewari, 1972; Saklani, 1972; Pachauri, 1972; Agarwal and Kumar, 1973; Validya, 1978, 1980; Rao and Pati, 1982, 1983; Islam and Thakur, 1988). It is characterized by multiple deformations resulting in superimposed folding and repeated faulting and thrusting.

At the top of the geological succession, in the upper reaches of the Mandakini River is the Precambrian Munsiari Formation composed of sericite-chlorite schist interbedded with sheared amphibolite and bands of mylonitized biotite rich porpyroblastic gneissose granite. The rocks of the later are separated from the underlying Bhatwari formation. The Bhatwari formation comprises biotite rich mylonitized quartz porphyry interbedded with schistose grey phylitte, diorite, greyslates, sericite quartzite with schistose phyllite, and granite porphyry. The rocks of Bhatwari formation occupy the larger part of the drainage area. The area is cut by numerous faults. Faults, fractures and joints are conspicuous in all rock formations and play an important role in promoting groundwater recharge and in locations of springs.

The Yamuna, the largest tributary to the Ganga originates at the Yamunotri glacier in the Higher Himalaya and drains the western part of the Ganga catchment. The river along with its major tributaries (Tons, Giri, Aglar, Bata and Asan) consists the Yamuna River Systems (YRS) in the Himalaya. The YRS drains a variety of lithology along its course (Gannser, 1964; Valdiya, 1980). The Yamuna, near its source in the higher Himalaya, drains mainly crystalline of the Ramgarh and the Almora Group, consisting of large masses of granodioritic-quartz dioritic rocks with abundant biotite and quartz, granites rich in tourmaline and muscovites. The metamorphics of the Almora in the Ramgarh Groups have occurrences of graphitic/carbonaceous schist and carbonaceous schists marble alterations (Valdiya, 1980). Further downstream, the catchment is characterized by slates, conglomerates, limestones, and dolomites (Valdiya, 1980). Downstream of the Lesser Himalaya, the Yamuna flows through the Siwaliks and finally the Indo-Gangetic Alluvium.

2.4 Ionic Composition or River Waters

The major ion chemistry of river water reveals the nature of weathering on a basin-wide scale that helps in understanding the exogenic cycles of elements in the continent-river system. Several studies have been carried out by various agencies over the past 3-4 decades on river water chemistry. For example, while monitoring river Ganga,

Subramanian (1987) pointed out that total dissolved solids (TDS) ranges from 105 to 209 mg/L. Bicarbonates and calcium are the two major constituents of river water constituting 57% and 23% by weight of TDS respectively. The next most abundant portion of the TDS are sulphate (5.3%), sodium (5%), magnesium (3.4%), and chloride (3%). Other ions are potassium, fluoride, and phosphate. Bicarbonates constitute 75-90% of anions while Ca+Mg constitute 68-93% of cations on equivalent basis. It is interesting to note that all the tributaries originating in Himalaya except Yamuna (which receives various tributaries draining through rocks different from those of the Himalaya) have high (Ca+Mg)/ (Na+K) equivalent ratios showing a weathering of carbonate rocks in the catchment areas.

Several workers have carried out extensive work over the last 3-4 decades on the anthropologically induced heavy metal pollution in the industrial region of the Ganga basin. Sediment and water samples have been collected in different periods of the year in order to analyze the variation in concentration and distribution of several heavy metals. For example, studies carried by Ansari *et al.* (1999) and Singh (1997) concentrated mainly on Cr, Mn, Co, Ni, Cu, Zn, Pb, and Cd.

In comparison to the study of trace metal concentration and distribution in the lowland industrial regions of river Ganga and Yamuna, very few studies have been conducted in the mountainous regions. Some work has been done by Purohit (2001) in Doon valley soil. The valley is surrounded by two major river systems, namely Ganga and Yamuna, on either side with a water divide passing nearly across the center of the valley. Their studies indicate that the heavy metal concentration in the fraction of –50 mesh (<75μm) of the Doon valley soils varies as follows: - Cr: < 4-413; Zn: 21-980, Pb: 5-165; Cu: 8-107: and Ni: 7-123 mg/Kg. The soils in the Ganga catchment sector are relatively more enriched in Cr and Ni as compared to that of the Yamuna. These features collectively indicate notable contribution from a mafic volcanic province in the upper reaches in the Ganga catchment, called Garhwal Volcanics (Kumar and Agarwal, 1975; Ahmad, 1998). The upper reaches of the Yamuna catchment are nearly devoid of mafic rocks. A strong positive correlation between Pb and Zn exists in the Ganga catchment where as in the Yamuna catchment the similar correlation is rather poor. The Cu concentration in the valley soils varies widely

from 8-107 mg/kg while the concentration of Cu in the Ganga and Yamuna catchment sectors are quite similar. Causative factor for such a sympathetic relationship may be ascribed mainly to the geological factors. The geological factors are commonly due to their strong chalcophile affinity that preferentially forms sulfide minerals under geochemical environments.

Presence of radioactive elements and their derivatives in the Himalayan springs has been reported by several workers (Chatterjee, 1978; Choubey *et al.*, 1997; Sarin *et al.*, 1990; Krishnasawmi *et al.*, 1999). The continuous movement of the Indian plate towards the Asian plate resulting in the rise of Himalaya eventually shows signs of intense neotectonic and seismic activity (Valdiya, 1980). Tectonic activity has developed a number of faults, fractures and joints in the rocks. Groundwater coming out in the form of springs and seepage from the disconnected local bodies of water through faults, fractures, joints and permeable layers get in contact with the underlying granitic and high-grade metamorphic bed rocks that has high concentration of Uranium, Thorium and Radium. The dissolved ^{238}U concentration in the Ganga and its tributaries ranges over an order of magnitude from 0.44 to 8.32 μg/L. The highland waters have $^{234}U/^{238}U$ close to equilibrium (about 1.05). The near equilibrium value of $^{234}U/^{238}U$ in the highland rivers is an indication that the uranium isotopes in these waters are derived from weathering of the catchments rocks. Since no accumulation of Uraniferous surficial sediments are known to occur in the study area, it is likely that these radioactive elements come from some nearby bedrock source through fault/thrust zone or fracture zone within the granite gneiss (Nashine, 1982). Interestingly Uranium mineralisation has been reported from shear zone of Bhatwari thrust having U_3O_8 from 0.037 to 0.78% in the form of pitchblende uraninite and fluroapatite associated with the sericite- biotite granite, peletic gneiss and sheared mylonites where most of the fault lineaments related springs are found (Nashine, 1982). Secondly in case of fracture joint related springs, the highly fractured and jointed rocks have increased the rock surface area to water volume ratio and thus increased the emanation efficiency with gases like radon (Lawerence, 1991). The hard rocks of Vaikrita, Munsiari and Bhatwari thrusts show pockets of high secondary porosity. Radon produced by isotopic decay of Uranium/Radium in catchment rocks are strongly adsorbed on fault breccias as remineralized matter along the fault surface. Being an inert gas, radon is redistributed and

dissolved in water when it flows through these zones. The high porosity and permeability facilitates the recharge and easy migration of radon to aquifers. Water thus enriched in radon ultimately comes out through the springs present along fault/thrust zones (Choubey and Ramola, 2000). The radon enters the groundwater from local source zone but does not accumulate in the spring water over the length of flow path (half life of radon is 3.8 d) because its radioactive decay rate is fast relative to the groundwater flow rate. The turbulent flow within such deposits is likely to cause natural de-emanation of gases, which find easy pathways through high porosity of the deposits from movement into the atmosphere (Choubey and Ramola, 2000).

Sarin *et al.,* (1990) carried out linear regression analysis in order to assess the relationship, if any, between dissolved uranium (^{238}U) and major cations (Na, K, Mg, and Ca) during weathering processes. The analysis shows that there is a strong positive correlation between them. Uranium is mobilized from solid phases to waters nearly to the same extent as cations (Na+K+Ca+Mg). The high intensity of weathering and mobilization of Uranium in the ^{230}Th-^{238}U disequlibrium is observed in the suspended phases. On an average there is 19% excess of ^{230}Th relative to ^{238}U in the suspended sediments. In oxic environments, such as in river waters, Uranium is quite soluble compared to Thorium. Hence Uranium would be leached out of solid phases and transported downstream as uranyl carbonate complexes where as ^{230}Th would be left in the solid phase (Langmuir, 1978).

Besides the Uranium and Thorium contents of the rock being weathered, several factors control the distribution of radium isotopes in river water. These include adsorption-desorption reactions on particle surfaces, supply of radium by dissolution, precipitation of insoluble phases, mixing of different water (including ground water), and decay of radium during transport (Krishnasawmi *et al.*, 1992; Rama and Moore, 1984). The radium concentration is not consistently related to other ions in the water. Unlike in the case of dissolved Uranium, there is no trend between either of Ra isotopes and major cations (Sarin *et al.,* 1990).

Black shales, are abundant in carbon, PGE and redox-sensitive metals such as U, V, and Mo (Horan *et al.,* 1994; Peucker-Ehrenbrink and Hannigan, 2000). Their oxidative weathering can also release these elements and CO_2 to the river waters draining them (Petsch *et al.*, 2000; Peucker-Ehrenbrink and Hannigan, 2000). The amount of CO_2 released from the Yamuna basin is about a factor of 2-3 times more than that from the Ganga. The CO_2 thus released results in precipitation of $CaCO_3$ which in turn scavenges the metals in these waters (Singh, 1999).

2.5 Microbial Activity in Ganga Water

Khanna *et al.* (1971) conducted an investigation to test in a scientific manner the folklore regarding the unusual 'keeping quality' of the Ganga river water even after long storage. Three most plausible reasons for rapid bacterial die-off, viz., the presence of radioactive substances, bacteriophages and transition metals possessing bactericidal properties, were investigated. They studied the effect of storage at room temperature (32-28^{0}C) on bacterial survival in the Ganga river water collected from Laxman Jhoola, Rishikesh, Uttaranchal, and compared that with bacterial survival in Yamuna river water collected at Tajewala, Jagadhari, Uttaranchal. Reduction in bacterial number in the Yamuna water was not completed even after 15 days of storage, where as a complete reduction was achieved in 7 days in the Ganga water. During the same period of storage the bacterial number in Yamuna water reduced only 10%. Using the limited data collected, they ascribed the unique keeping quality of the Ganga river water to the presence of bacteriophages in the water and heavy metals in the riverbed. Prasad (1977) in his studies on coliform survival in the Ganga River near Kanpur suggested that the apparent rapid coliform die-off is owing to suspended solids, heat labile and to some extent high concentration of organic matter.

Studies reveal that despite high organic pollution load in River Ganga, it maintains the low BOD and high DO levels (Tare *et al.*, 2003; Bhargava, 1977). The rapid depletion of BOD after covering some distance downstream has been ascribed to bio-flocculation mechanism in which the exocellular polymers excreted by the various species of bacteria in the

endogenous phase act as excellent coagulants (Bhargava, 1977; Pavoni *et al.*, 1972). These coagulants are reported to be effective in flocculating the finely divided inorganic and organic matter and thereby removing them through settling to the bed.

Bhargava, (1977) studied the water quality of rivers Ganga and Yamuna at few selected locations. The DO value in both the rivers at Rishikesh and Dakpattar during winter and summer was ~ 8 mg/L. The coliform levels during winter and summer in Ganga R. were 100 and 11 per 100mL respectively. The corresponding levels in Yamuna R. were >2400 and 70 per100mL. The results revealed that biological growth in Yamuna R. exceeded that in Ganga R. in both the seasons.

2.6 Concluding Remarks

The review of literature presented reveals that sufficient information is available to explore the issue of superior keeping water quality of the river Ganga. However, very few scientific studies have been attempted to address this issue. While a lot of scattered information is available pertaining to the geochemistry and physico-chemical quality of the Ganga River on one side and the role of aquatic chemistry in controlling the microbial activity in river waters that can plausibly influence the keeping quality on the other side, studies synthesizing the two aspects are warranted.

3. Objective and Protocol

River Ganga is considered to be the most sacred river. It is believed that the water of the river Ganga has some special characteristics which allows storage over a prolonged period without deterioration in quality. A few limited scientific observations and investigations support this belief. Despite the most crucial river of the country with religious importance, few scientific studies have been taken up to develop understanding on river water quality. Very scanty and scattered information is available in terms of river water chemistry. The presence of trace metals and radioactive elements in water and sediments of the river Ganga in concentration beyond the threshold value for sustenance of aquatic life seems to have played a pivotal role in maintaining the virginity of the river. The review of literature (Chapter 2) reveal that substantive information is available on the lithology, weathering reactions and its influence in governing the water chemistry of the rivers, particularly Ganga and Yamuna.

On the other hand substantial efforts have been made to understand the role of metal ions and radioactive elements on microbial activities in the aqueous environments. The bactericidal properties of irradiation have been known for a long (Lowe et al., 1956). Ancient Asiatic and Mediterranean peoples seemed to have knowledge of the beneficial properties of trace metals. However, no thorough study of these properties was made until the work of the Swiss botanist Nageli in about 1893. Nageli termed the germicidal effect as oligodynamic. The term derives from the Greek oligos (few) and dynamic (power), and refers to the apparent power of very minute concentrations of trace metal ions to kill organisms (Addicks, 1940). Some of the very early studies report probable interaction of metal ions with cell matter to cause protein coagulation (Frobisher, 1957). The metal – microbial interactions, however, are not yet fully understood. A large number of data concerning toxicity of trace metals on various aquatic organisms has been collected. Very few attempts have been made to explore such information in systematic manner to study microbial activities in natural river water systems.

Investigations on the effect of trace metals and radiations out of radioactive particles on aquatic life in the river Ganga may unveil certain aspects that could help in explaining

observations regarding unique keeping water quality. It is contended that such a study would be meaningful if conducted in the upper stretches (in the hilly region) of the river where the impact of anthropogenic activities is minimal. The present study is thus essentially aimed at analyzing the river water quality in terms of chemical composition with emphasis on presence of trace metals and radioactive elements vis-à-vis the available information regarding the impact on microbial activity in the aquatic environments. Following research protocol is adopted to achieve the aforementioned objective.

- Selection of the stretch of river Ganga and other Indian rivers for comparative assessment.
- Collation of available information regarding sediments and water chemistry of chosen rivers in the selected stretches.
- Gathering information regarding certain physico-chemical parameters such as temperature, pH, dissolved oxygen, hardness, organic content, heavy metal content and presence of radioactive elements through analysis of water samples from selected locations.

- Comparison of the distribution trace metals in water and bed sediments amongst various Indian rivers.
- Comparison of the distribution of radioisotopes of U and Ra in water and U and Th in bed sediments of the major Indian rivers as well as some rivers of the other countries.
- Collation of information regarding the influence of pH, temperature, dissolved oxygen, alkalinity, hardness, major cations and anions, and dissolved organic matter on the uptake and bioaccumulation of trace metals by the aquatic microbes.
- Assess the effect of trace metal concentrations in water and radiation from radioisotopes in aquatic life based on available information.
- Develop and compare overall impact factor for inhibition of microbial activity in the waters of selected Indian rivers that may unveil some information regarding reported unique keeping water quality of the river Ganga.

4. Methods

In order to substantiate the contention that water of the river Ganga has some unique keeping quality a comparative assessment of the water quality of the selected Indian rivers was planned. Three Indian rivers, namely Yamuna, Godavari and Narmada were chosen besides the river Ganga. The river stretches/locations chosen were close to the river origins to keep the interference of anthropogenic action to minimal level. The study was divided into four parts.

The first part involved compilation of the information on river water quality from the literature and the data available through various studies by different workers. Some work has been done on river Ganga. However, very few studies have been conducted on river Yamuna, Narmada and Godavari. Most of the studies were conducted from the point of view of water pollution and hence focused on the selected polluted stretches of these rivers. A comprehensive study at or in the vicinity of the respective origins of the rivers has not been reported.

The second part of the study intended at collection of primary data essentially aimed at generating additional information related to estimation of concentrations of trace metals and radioactive elements in water and bed sediments of these rivers.

The third part of the study involved collation of information regarding the influence of trace metals and radiation from radioisotopes dissolved in water on aquatic organisms present in the river water. This took into account experiments conducted by other researchers concerning toxicity/lethal doses of trace metals and radiations with varying physico-chemical factors.

The fourth part of the study aimed at comparative assessment of river water quality of selected rivers vis-à-vis impact on microbial activities. Attempt has been made to assign impact scores following techniques used for assessing toxicity to microbial populations in aqueous systems giving due considerations to physico-chemical factors.

4.1 Compilation of the Available Information

The information related to water quality of the four rivers at their sources has been divided into three groups. The first group consists of available information related to water quality parameters of the river at specified locations at different times. The second group consists of very limited data related to trace metal concentrations in waters of the rivers Yamuna, Narmada, and Godavari. The third group consists of limited data collected to assess the impact of trace metals and radiation out of radioisotopes in aquatic organisms.

4.1.1 Group I: River Water Quality Data

Several researchers have attempted to assess the water quality of Indian rivers through estimation of various water quality parameters. Emphasis in most of the researches was on determining the extent of river pollution. A listing of the information available and scanned for purpose of this research is presented in Table 4.1.

4.1.2 Group II: Data Related to Trace Metal Concentrations in Water and Bed Sediments of the Four Rivers at their Respective Sources

Scanty information is available on the trace metals concentrations in river water and bed sediments of these rivers at their respective sources. Some systematic, but limited, study was conducted on river Ganga. The water quality of the river Ganga was assessed by collecting samples at the point at which the two rivers meet, commonly called 'Prayag'. Very few studies were also done on rivers Yamuna, Godavari, and Narmada at their sources. A listing of available information that could be meaningfully used to satisfy the objectives of the present studies has been included in Table 4.1.

Table 4.1: Listing of Available Information on Water Quality for Four Rivers

Period	Monitoring Period	Monitoring sites/location	Parameter studied	Reference
1977	Monsoon	Ganga River (Haridwar to Calcutta)	pH, conductivity, major cations and anions, silica, TSS, discharge, erosion rate	Subramanian (1979)
1982-1983	March, September, November, December	Ganga and Yamuna head water	pH, conductivity, major cations and anions, silica, TDS and clay minerals	Sarin (1989)
1981	Monsoon	Ganga River (Haridwar to Calcutta)	Alkalinity, major cations and anions, silica, TDS, clay minerals and heavy metals in bed sediments	Subramanian (1987)
1980	October, December	All major rivers of India	Alkali metals, alkaline earth metals, transition metals and radioactive elements in sediments	Subramanian, (1984)
1998-1999	October, June, September	Yamuna headwater	Major cations and anions, TDS, Si, F, Cl, carbon (%),	Dalai *et al.* (2002a)
1983-1995	Not Available	Doon Valley (Ganga, Yamuna catchment)	Heavy metals in sediments	Purohit (2000)
1985-1986	October, April	Ganga head water	Heavy metals in water and bed sediments	Saikia, (1988)
1978-1979	June, August	Godavari and major tributaries	Alkali metals, alkaline earth metals, transition metals and radioactive elements in sediments	Biksham *et al.* (1988, 1991)
1984	August	Krishna and major tributaries	Alkali metals, alkaline earth metals, transition metals and radioactive elements in sediments	Ramesh, (1990)
1999-2002	Not Available	Ganga, Indus river (lesser Himalaya)	Uranium and Thorium in sediments	Singh *et al.* (2003)
1998-1999	October, September	Ganga and Yamuna headwater	Major cations and anions, Re, Os, U in sediments	Dalai *et al.* (2002b)
1982-1983	March, September, November	Ganga and Yamuna headwater	U, Th and Ra isotopes in sediments	Sarin *et al.* (1992a)
1997	Not Available	Garhwal Himalaya	Radon in water	Choubey *et al.* (2000)
Not Available	Not Available	Bhagirathi-Alaknanda River system	U, Ra	Sari *et al.* (1992)
1975-1979	Not Available	Narmada, Tapti and major tributaries	U isotopes in river	Borole, (1981)

4.1.3 Group III: Data Related to the Impact of Trace Metals and Dissolved Radioisotopes on Aquatic Organisms

Trace metal concentrations below a certain value are useful for the metabolic activities of aquatic organisms. However, their concentrations above a certain value have detrimental effect. Chronic exposures to such a concentration influence the metabolic activities of these organisms and in turn may be fatal. Similarly, prolong exposure to radioisotopes and its radiation affects cell growth. Different workers conducted several separate studies involving different organisms. Most of the works has been done on a particular test organism under the influence of a single metal. However, few studies have been done on the combined effect of several metals present in the system. All such data have been used in the comparative assessment of the impact on the microbial activity in the river waters with appropriate citations.

4.2 Collection of Primary Data

The principal objective of this phase of the study was to supplement the available data regarding trace metals and radioactive elements in river water and bed sediments. Field and laboratory studies were carried out that involved sampling and analysis of water and sediments in four Indian rivers.

Description of the selected sites: Sampling sites were selected such that the anthropogenic influences are minimal. In order to get the background information on river water quality of these rivers, the sites were selected in the vicinity of their origin to some distance downstream. The river Ganga gets its name at Deoprayg where river Alaknanda and Bhagirathi intermingle. However, before this, the above stated river flows through several 'prayag' where it meets with some other big rivers. All rivers meeting the river Ganga in the hilly stretch originate from the Himalaya but flow through different regions. The rivers after culminating at Deoprayg flow as Ganga down stream towards Rishikesh followed by Haridwar, and towards the plain. The other three rivers, viz. Yamuna, Godavari, and Narmada, are short streams in comparison to the river Ganga. River Yamuna, a major tributary of the river Ganga before meeting the later at Allahabad, flows as a separate stream. The river Yamuna originating from the Himalaya is a narrow and

steep channel. The water and sediment samples of river Yamuna were also collected from its origin to several kilometers downstream. The water and sediment samples of rivers Godavari and Narmada were collected mainly from different locations of Nashik and Jabalpur respectively. Overall, twelve sites were selected for sampling on river Ganga, four over Yamuna and the three each for rivers Godavari and Narmada. The locations of the sampling stations are given elsewhere.

Sampling: Samples were collected at different times during May 2003 to January 2004. Rivers Ganga and Yamuna were sampled twice: once during May-June 2003 and once in mid November 2003. Rivers Godavari and Narmada were sampled once during mid January 2004. All water samples were collected at 0.5 m below the water surface and bed sediments from 0.5 m below the surface. Estimation of temperature, pH and DO were done on site immediately after the collection of the samples. 1 L grab sample of water was collected in torsion bottles. 10 g bed sediments in plastic bottles and a handful of rock chips were also collected from each of the locations. The water samples were acidified with 1.5 mL HNO_3 and brought to the Environmental Engineering Laboratory, Department of Civil Engineering, IIT Kanpur, India. The samples were filtered and stored in refrigerator. The samples were analyzed following the analytical techniques mentioned in Sectiȯn 4.2.

4.3 Analytical Techniques

Most of the analytical techniques followed were of routine type and were conducted as per the Standard Methods for the Examination of Water and Wastewater (APHA *et al.*, 1995). A listing of such techniques along with instruments used, name of the method, reference, etc. is presented in Table 4.2. Techniques for trace metal analysis for water and bed sediments, and that of gross alpha activity of radioisotopes in water as adopted in this study are briefly described as follows.

Estimation of Trace Metals in Solid Samples: To determine the heavy metal concentrations in solid samples, the samples were dried at 105^0C. The dried sample was sieved. 1.0 g of the sample was placed inside a 30 mL Kjeldahl flask. 15mL of aquaregia

was added to it and swirled for 5 minutes. After 12 h, the flask was placed in the heating block at 50^0C for 30 minutes. The temperature was raised to 120 ^0C and heated for 2 h. 10 mL 0.25 M HNO_3 was added after cooling to room temperature. The sample was then filtered through Whatman No. 541 filter paper. The flask was washed properly several times and the contents were transferred to a 50 mL torsion bottle. The bottle was filled up to the mark with 0.25 M HNO_3. The samples were analyzed by AAS, Varian 220 FS.

Estimation of Trace Metals in Liquid Samples: To determine the trace metal concentrations in water samples, 100 mL of the thoroughly mixed water samples were taken in a narrow neck round bottom flask. 5mL concentrated HNO_3 was added. The sample was heated at 120 ^0C in a heating block until the volume of the water reduced to 5 mL. The contents of the flask were transferred to a 50 mL torsion bottle with several washings. The bottle was filled up to the mark with 0.25 M HNO_3. The samples were analyzed by AAS, Varian 220 FS.

Estimation of Gross Alpha Activity: For Gross alpha activity of water, 500mL of water sample was concentrated to 200 mL on heating at 120 ^0C. While heating 30 mg Fe^{+3} and 7 mg Ba^{+2} carrier was added. The sample was cooled to room temperature. 1:1(v/v) H_2SO_4 was added to the sample. The resultant mixture was stirred and neutralized with addition of aqueous ammonia. Stirring was continued for some time. The precipitate of $Fe(OH)_3$ and $BaSO_4$ thus formed were dissolved in 1:1 (v/v) HCl. 1 mg La^{+3} carrier was added to it and was transferred to a polythene centrifuge tube. The precipitate thus formed, was added HF, and 1 mg glacial acetic acid. After centrifuging and washing with water, the precipitate were transferred to a stainless steel planchet and heated under IR rays. The film thus formed was finally flamed over a gas oven. The planchet prepared was put in an Alpha Scintillation Counter (ZnS-Ag) for counting.

Table 4.2: Analytical Methods Employed for Water Quality Analysis

Parameter	Method Used	Instrument Used	Reference
Dissolved Oxygen (DO)	Winkler Method with Azide Modification		Standard Methods, APHA *et al.*, (1995)
pH	Glass Calomel Electrode	Digital pH Meter	
Temperature		Thermometer	
ORP		Eh Electrodes, Ag/Agcl Electrodes	Standard Methods, APHA *et al.*, (1995)
Ca, Mg, K, Na		AAS Varian 220 FS	Standard Methods, APHA *et al.*, (1995)
Sulphate (SO_4^{-2})	Turbidimetric		Standard Methods, APHA *et al.*, (1995)
Bicarbonate (HCO_3^-)	Acid Titration		Standard Methods, APHA *et al.*, (1995)
Chloride (Cl^-)	Argenotometric		Standard Methods, APHA *et al.*, (1995)
Hardness	EDTA Titrimetric		Standard Methods, APHA *et al.*, (1995)
Alkalinity	Acid Titration		Standard Methods, APHA *et al.*, (1995)
Conductivity		Conductivity Meter	Standard Methods, APHA *et al.*, (1995)
TOC	Combustion Infrared (Pt catalyst)	TOC-VCP N Shimadzu	Standard Methods, APHA *et al.*, (1995)
U, Th, Ra in sediments	Cr-Kα target	XRD	
Gross alpha activity	Co-precipitation	Alpha Scintillation Counter	
Trace metals in water	Nitric acid digestion	AAS Varian 220 FS	Standard Methods, APHA *et al.*, (1995)
Trace metals in sediments	Aquaregia digestion	AAS Varian 220 FS	Standard Methods, APHA *et al.*, (1995)

5. Results and Discussion

5.1 General

The present research was aimed at gathering scientific information for critically examining the contention that water of the river Ganga has distinguishing composition that could be attributed to its unique "keeping quality". To achieve this aim, some specific aspects of the physicochemical characteristics of water in the virgin stretches of the river Ganga were assessed and compared with those of the other three important Indian rivers. The river stretches in the vicinity of their origins were selected to circumvent the influence of anthropogenic activities. Thus it is assumed that the variations in selected physicochemical characteristics of the river water are solely due to water-rock interactions, and are directly influenced by the general lithology of the drainage basins.

5.2 Hypothesis and Approach

It is hypothesized that the "keeping quality" of river waters is related to the sustenance of microbial activities which in turn is governed by the physicochemical characteristics of the water. Thus it is argued that the contention of Ganga water possessing unique qualities could be supported if it has much higher potential to apprehend the biological growth than the waters of other rivers. The following approach has been followed to test the hypothesis.

- Collation of lithological aspects of the drainage basin in the selected river stretches.
- Collation of some physicochemical characteristics of the river waters in the stretches of interest.
- Field studies to collect primary data on (i) lithology of drainage basins in the study areas and (ii) physicochemical characteristics of the river water with emphasis on trace metal content, presence of radioactive elements, and levels of dissolved carbon and cations to supplement the available information.

- Collation of information on growth limiting factors and perniciousness to aquatic microbial activity.
- Assigning impact scores for apprehending microbial activity in river waters based on estimated specific physicochemical parameters.
- Integration of the influence of various factors to arrive at the overall impact score as sum total of the individual effects, and comparison of the overall impact scores for apprehending microbial activity in waters of selected rivers.

5.3 General Description of the Selected River Stretches

Three rivers, namely Yamuna, Godavari and Narmada have been selected for comparison purposes to bring out the uniqueness, if any, of the water of the river Ganga. The river Yamuna, although originates from the Himalayan Glaciers as that of the river Ganga, intermingles with various tributaries which flow over different rock types in the upper course. Rivers Narmada and Godavari, flow over an entirely different geological area, are expected to have different water chemistry compared to that of the Himalayan Rivers. Figure 5.1 shows the trace of the four rivers included in the present study on a map of India. Selected stretches/sampling locations have been marked on this figure.

River Ganga originates at Gaumukh from the icy glacial deposits of Gangotri as 'Bhagirathi' at an elevation of 3042 m, latitude 31^0N and longitude 78^0E and crisscrosses the Greater Himalayas over a distance of 259 Km. It is joined by Alakananda at Deoprayg, and the combined stream under the name Ganga flowing through mountainous regions debouches into the plains at Rishikesh.

The river Yamuna originates at Yamunotri at an elevation of 3165 m, latitude 30^0N and longitude 77^0E. It is one of the largest tributary of the river Ganga draining the southern slopes of the Himalayas. The river merges with the river Ganga at Allahabad in the Gangetic plains.

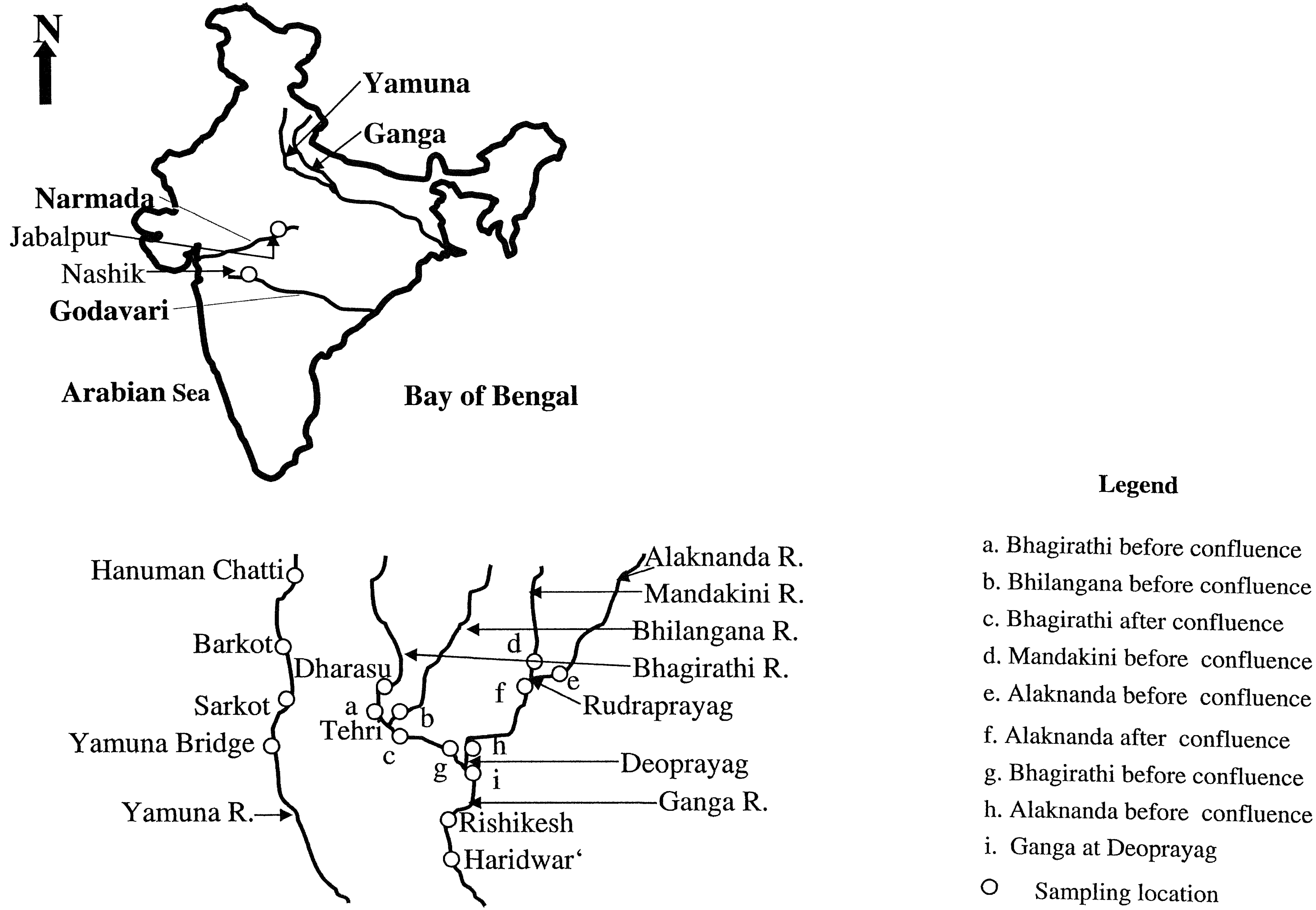

Figure 5.1 Schematic Representation of the Selected River Stretches

The Godavari River carries an enormous sediments load (170 million tons/year; Bikshan and Subramanian, 1988), and is the largest in the peninsular India. The Godavari basin (16^0N to 18^0N latitude and 73^0E to 83.3^0E longitude) covers an area 313,147 Km ^{2} in the central and the southern part of the Indian subcontinent. The river originates from Nashik in Western Ghats and travels 1,465 Km before emptying into the Bay of Bengal. The mean elevation of the basin is 420 m. The Narmada River located in central India originates at 'Amarkanthak'. The river flows over the Deccan traps and finally debouches into the Arabian Sea (Krishnan, 1966).

The four rivers either originate from different sources or originate from the same source but flows through different rock types and accordingly their water chemistry changes. The water chemistry of these rivers at the studied area is largely governed by the geological formations. Some general information regarding the rock types is presented in Table 5.1.

Table 5.1: General Description of the Rock Types in the Drainage Basins of the River Stretches Selected for the Study

River Catchments	Rock types	Reference
Ganga River	Carbonates, Sandstone, Slates, Shales, Granite, Quartizite, Orthoquartzite, Conglomerate and Geniss of different age groups.	Gannser, (1964); Valdiya, (1980)
Yamuna River	Carbonates, Sandstone, Slates, Shales, Granite, Quartizite, Orthoquartzite, Conglomerate and Geniss of different age groups.	Gannser, (1964); Valdiya, (1980)
Godavari River	Deccan traps, Archean granites, Precambrian and Gondwana sedimentary rocks	Bikshan and Subramanian (1988)
Narmada River	Rocks of late Archean to early Proterozoic greenstone belt, overlained by Upper Proterozic Vindhyan sediments	Krishnan, (1966)

5.4 Comparison of Trace Metals Content in Water and Riverbed Sediments

Nine trace metals were selected based on the studies by earlier workers and their ability to apprehend microbial growth. The concentration of these metals in the four rivers were compared and represented separately. Figure 5.2 shows that Ganga water is enriched in almost all the metals compared to that of the other rivers. Yamuna water has concentration higher than that of the other two rivers.

Some researchers have estimated the concentrations of heavy metals in riverbed sediments of major rivers in India at different times and at different locations. It has been found that the concentration of almost all the trace metals in Ganga sediments is less than that of the other rivers. Figure 5.3 reveals the difference in metal concentration in different rivers of India. It is interesting to note that despite lower concentration of metals in the bed sediments, the Ganga water is highly enriched in all the metals.

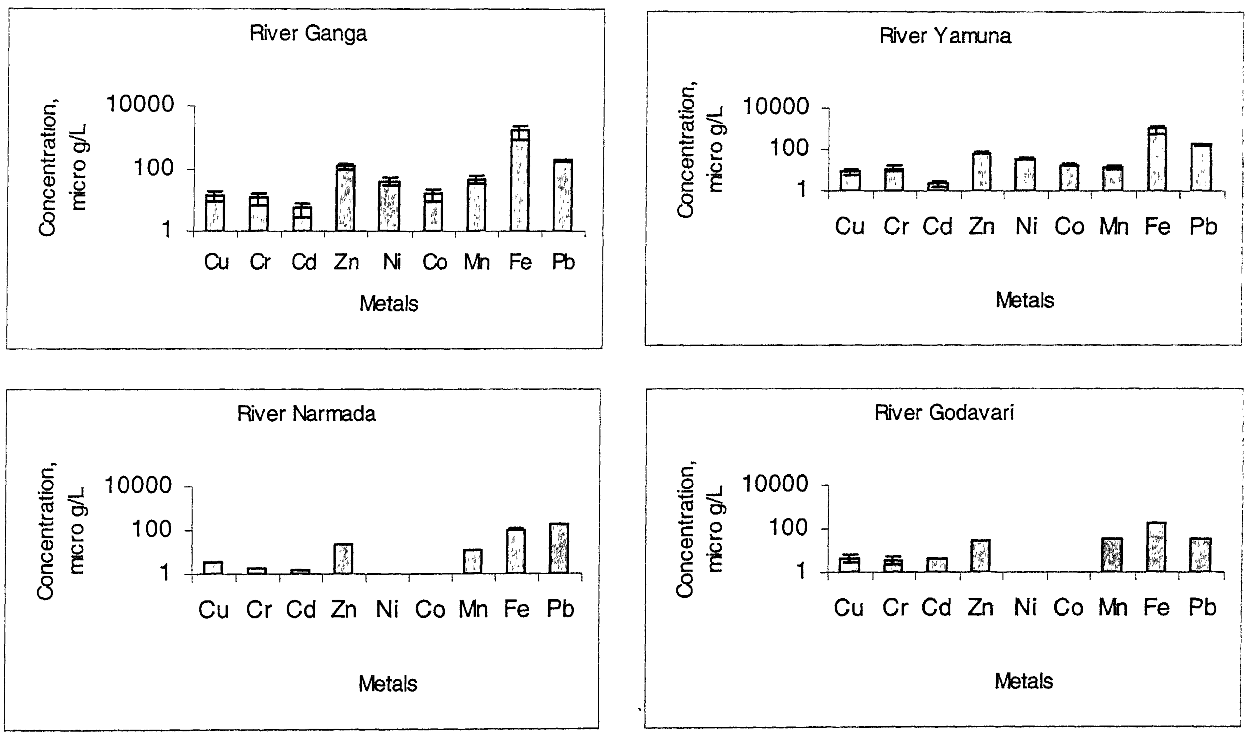

Figure 5.2: Mean and Range of Trace Metals Concentration in Some Indian Rivers

The distinct difference in the water chemistry is attributable to the differences in the geology of their drainage basins, grain size and type of weathering processes. Gibbs (1967) pointed out that the elevation is the most important factor controlling the erosion in river basin. However, for the Ganga River, the elevation is negatively correlated with the sediment erosion rate. The sediment erosion rate is higher in Ganga river compared to that of the Yamuna river despite the fact that later originates at higher elevation (Subramanian, 1987). Rivers Godavari and Narmada have much lower gradient compared to that of the Himalayan Rivers, and hence have lower weathering processes and lower dissolution of trace metals.

The dissolution of a particular trace metal during weathering depends on the mineral in which the element occurs, and on the intensity of chemical weathering (Harriss and Adams 1966; Kronberg 1979). They may be present in major minerals of the rocks or in chemically resistant accessory minerals such as zircon, apatite or monazite, or as sulfides. The resistant minerals generally remain unaltered unless weathering is very intense, and so alteration of them never causes high metal concentrations in water (Samuel and Osman, 1981).

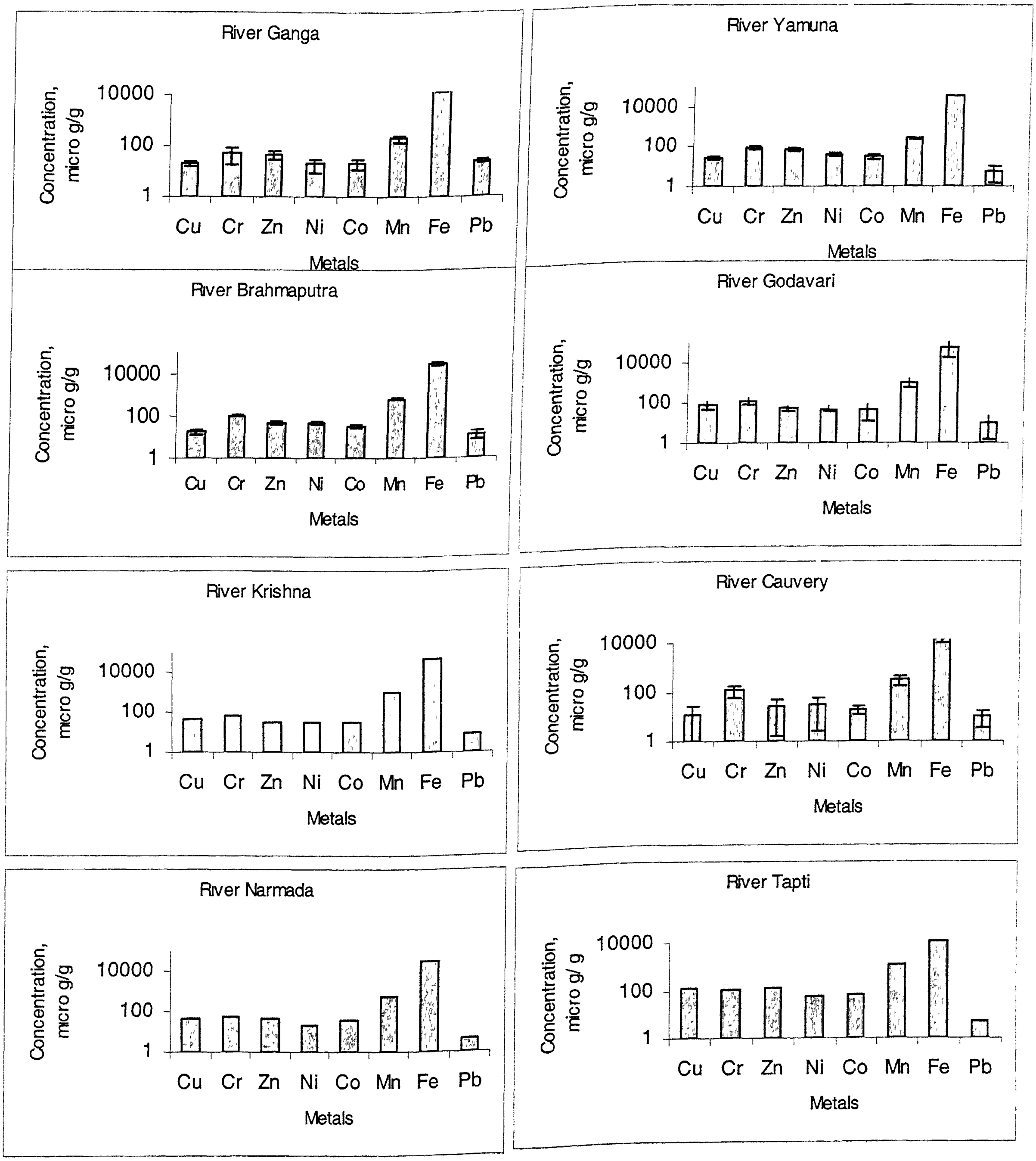

Figure 5.3: Mean and Range of Trace Metals Concentration in River Sediments. Rivers Ganga and Yamuna in Himalayan Region (Present work) and Remaining from Subramanian *et al.* (1985)

In the absence of a detailed study of the rock types at every location not much can be inferred regarding the presence of trace metals in the river waters based on sediment erosion rates alone.

The low concentration of trace metals in Godavari and Narmada waters might be due to the fineness of the grains. The transition elements precipitate as oxyhydroxides and get locked up in fine suspended particles. This leads to higher metal content in the sediments. On the other hand, the low trace metal content in Ganga sediments is may be due to the presence of coarser (0.5-1.0 mm) fractions. However, the Yamuna bed sediments contain much coarser (1.0-2.0 mm) fraction compared to that of the Ganga sediments and yet contain higher levels of trace metals. (Whitney 1975; Chao and Theobald 1976; Tessier 1982) have revealed that larger particles stay in a place longer, often in shallow oxygenated areas of streams and therefore may have more time to develop oxide coating. This in turn may adsorb more trace metals from the liquid phase than the smaller particles. This may be the plausible reason for higher metal content in bed sediments of the river Yamuna. The trace metal concentration in Yamuna water is; however, lower in comparison to the Ganga water.

A dramatic increase in adsorption of metals with release of hydrogen ions in solution is observed with increasing pH. A study by Gạdde (1974) shows that the adsorption of Pb, Cd, and Zn on hydrous Mn (IV) oxide was favored with increased pH. At pH 7.5 - 8.0 more than 90% adsorption occurred in hydro-Mn where as in hydrous ferric oxide at pH 7.8 –8.0, Pb(II) and Zn (II) adsorption was more than 90 % and Cd (II) adsorption was about 60%. The extent of adsorption at pH 8.0 lies in the order of Pb> Zn> Cd.

The pH of the water in the four rivers studied varies in the range 7.8 – 8.2. However, they vary in terms of Fe and Mn content in the bed sediments. The higher concentrations of Fe and Mn in the bed sediments of rivers Yamuna, Godavari and Narmada compared to that of the river Ganga clearly indicate an increased precipitation of hydro-Mn and hydrous ferric oxide. This in turn may be responsible for higher adsorption of metals from waters.

5.5 Comparison of Dissolved Organic Carbon in Water

The affinity of trace metals for organic substances and their decomposition products is of great importance for the behavior of trace metals in aquatic systems. Organic matter plays an important role in the distribution and dispersion of trace metals in the secondary

environment by mechanism of chelation and cation exchange (Forstner 1983). Reaction between a metal ion and an organic ligand in solution leads to a species that can either precipitate directly or be adsorbed in sedimentary material.

The Total Organic Carbon (TOC) levels in the waters of the four rivers in the selected stretches/locations are presented in Figure 5.4. The Ganga water has much lower dissolved organic carbon compared to that of the waters of other rivers. The Ganga water being low in organic substances provides less possibility of formation of organo-metal complexes.

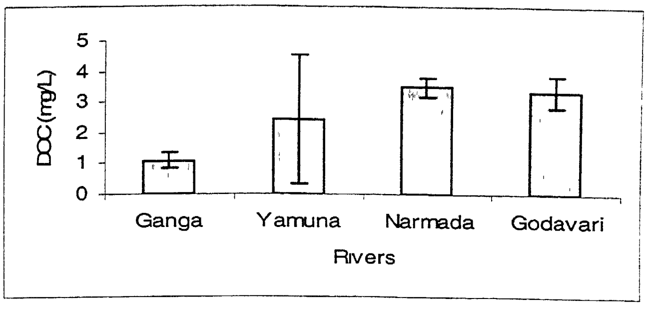

Figure 5.4: Mean and Range of Dissolved Organic Carbon in the Waters of Four Rivers Selected for the Study

5.6 Comparisons of Radioisotopes in Bed Sediments and in Water

Natural radioisotopes in water are derived from rocks and minerals with which the water remains in long contact. Both qualitative and quantitative methods have been followed to find the presence and estimate their concentrations in the bed sediments of various major rivers in India. Results presented in Figure 5.5 reveal that the Himalayan Rivers are more enriched in Th than the other major rivers. Godavari closely follows both the Himalayan rivers. However, the U content is almost the same in sediments of all the rivers except in those of the river Cauvery, which shows slightly lower values.

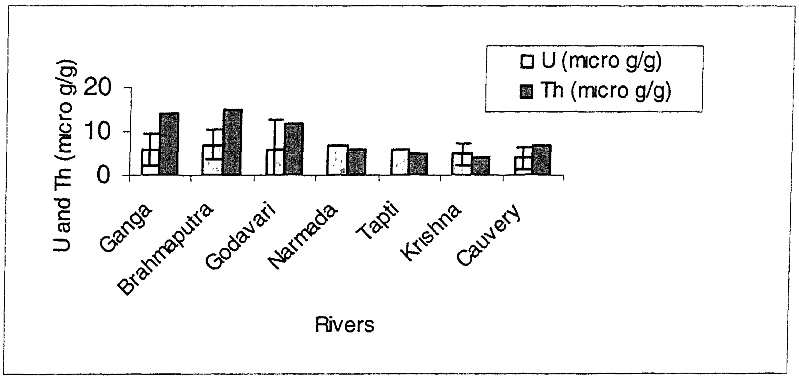

Figure 5.5: Uranium and Thorium Concentration in River Bed Sediments of Some Indian Rivers. Data Taken from Subramanian *et al.* (1985)

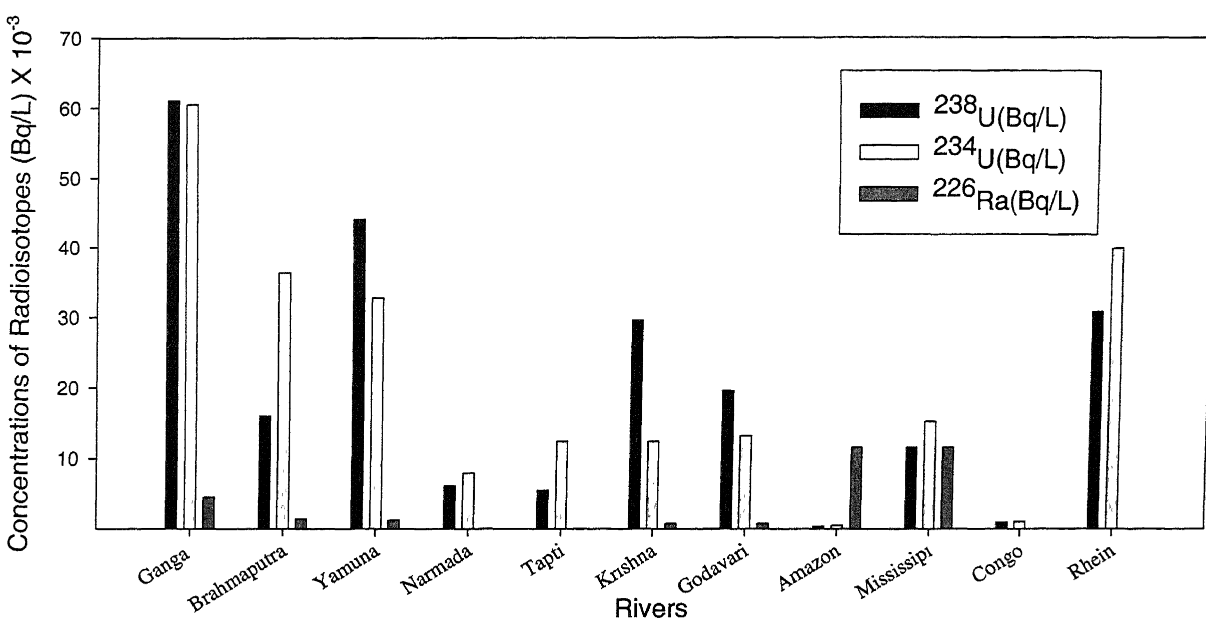

Figure 5.6: Mean Concentration of Radioisotopes in Some Major Indian Rivers and of the World (Sarin *et al.*, 1992; Borole *et al.*, 1981; Moore, 1967; Martin *et al.*, 1978b; Mangini *et al*, 1979).

Figure 5.6 reveals that Ganga water has a much higher concentration of both ^{238}U and ^{234}U. Yamuna water follows the Ganga water in ^{238}U content. The concentrations of ^{234}U in other rivers are far below that of the Ganga water. However, the ^{226}Ra concentrations in all the rivers are almost the same and are quite smaller than that of the U concentrations. A similar comparison has also been made between major Indian rivers and that of the

world. Figure 5.6 show that the Ganga water outmatches the waters of other rivers. The concentrations of radioisotopes in water of Congo and Amazon rivers are significantly lower compared to that of the Ganga water.

In oxidized environments, U exists as the highly soluble uranyl $[U(VI)O_2^{+2}]$ species. Uranium forms soluble complexes with carbonate, oxalate and hydroxides (Grenthe 1992). In the absence of high levels of complexing ligands, dissolved uranium sorbs to Fe oxide minerals and organic matter over a wide range of pH conditions. However, Ganga water is impoverished in both Fe and Mn content in bed sediments and also has low TOC values compared to that of Yamuna, Godavari and Narmada waters (Figure 5.3 and 5.4). A quantitative study was also carried to find the gross alpha activity of the Ganga and Yamuna waters. The study includes the entire alpha emitting radio nuclides of U, Th and Ra. The results show that the concentrations in Ganga and Yamuna waters are in the range 27-100 mBq/L (mean 70 mBq/L) and 16-37 mBq/L (mean 26.6 mBq/L) respectively.

5.7 Metals-Microbe Interactions

The aquatic chemistry of trace metals in the natural environment is dependent on the distribution dynamics of the metals and on the types of interactions between the metals and their aquatic habitat (Mancy *et al.,* 1976). The physicochemical characteristics of the aqueous phase, the interaction with organic and inorganic compounds of suspended and sedimentary solid materials (Guy *et al.,* 1975; Guy *et al.,* 1976), and the availability of both inorganic and organic complexing agents (Gardiner 1976) can greatly influence the distribution of trace metals and their subsequent effect on aquatic biota. The cellular bases are almost exclusively sulfur, nitrogen, and oxygen donor groups including H_2O and solute bases like HCO_3^{2-}, HPO_4^{2-}, and OH^- (Stumm and Morgan, 1981). In natural waters the metals readily form stable hydroxy or carbonate complexes, or both, and only a fraction of the total concentration exists as the cationic or aquo form (Stumm and Morgan, 1981).

Microbial populations usually secrete large amount of extracellular exopolymers (EPS). This is a highly hydrated material (~ 99% water) possessing an extremely porous fibrillar

structure that renders it highly adsorptive. The polysaccharides of EPS possess abundant anionic carboxyl and hydroxyl groups that provide potential binding sites for metals. Microorganisms adsorb and concentrate many metallic cations required for growth through electrostatic interactions with anionic carboxyl and phosphoryl groups in the cell wall (Konhauser 1993). EPS can bind a wide variety of metals at pH 8 (Ferris, 1989).

A fascinating aspect of metal-microbe interactions is the ability of the microbial cell to deal with the range of metals required for growth and function. The supply of metals to the cell depends upon several external factors such as concentration of the metal in the local environment and also its bioavailability. The later factor is related in turn to the solubility of the metallic species and to the presence and properties of any ligand to which the metal cation may be complexed. Uptake of a specific metal from the environment is then under the control of the cell, which is able to distinguish one metal from another, and to provide specific transport systems for their translocation to certain intercellular sites. Other metal cations are necessarily excluded from these sites. This precise control of metal binding in biology contrasts with a simple chemical situations, where the competition between the metal ions for a ligand is normally own by the metal ion which is the strongest Lewis acid of those present. Thus, if a range of biologically important metals were presented with a variety of ligands, then Cu (II), as the strongest Lewis acid, would dominate the competition for ligands. No other metal ion would bind until the concentration of free Cu (II) had been lowered by complexation to a range where other metal ions would be able to compete. Yet, in contrast the cell is able to select a metal such as Ni (II) or Zn (II) in the presence of Cu (II) and insert it into an appropriate site. This ability to bind one metal from a range of competing cations is a remarkable example of selectivity˙ (Huges, 1989; Williams, 1981).

Metals are classified into two groups, Essential metals that include Na^+, K^+, Ca^{2+} and Mg^{2+} and are present in relatively high concentrations in biological systems and may be classified as bulk metals. They are distributed selectively, with K^+ and Mg^{2+}concentrated inside the cell and Na^+ and Ca^{2+}outside the cell. This selective distribution is fundamental to the biological functions of these four cations (Huges, 1989; Williams, 1981). The d block elements are present often at an extremely low level and are usually described as the trace and ultra trace metals. This group includes the 3d transition metals from V through

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Zn (V, Cr, Mn, Fe, Co, Ni, Cu and Zn) and Mo. The essential metals may also exert toxic effects by binding to other sites. They usually bind most strongly to sulphur containing groups.

In general, these three groups of metals, the bulk essential metals, the trace essential metals and the toxic metals, prefer different ligand groupings (Huges, 1989; Williams, 1981). For example Cu (II), the strongest Lewis acid amongst the essential metals, is dominant in competition among the trace metals for ligand sites. However, it has been found that in certain circumstances weak Lewis acid such as Mg (II) competes against Cu (II). This is achieved because Mg (II) has a higher affinity for oxygen donor atoms, for which Cu (II) has lowest affinity. The binding of Mg (II) is favored further because it is present in much higher concentrations than Cu (II). If the two metals were competing for the ligand environment that included nitrogen or a sulphur donor atom then the result would be reversed, irrespective of this concentration factor.

The affinity of a metal ion for a particular ligand environment depends upon several factors. For biological activity to be maintained, the replacement metal ion should bind to the site in as similar a fashion as possible as the native metal. To achieve such 'isomorphous' substitution, both native and replacement ions should have the same ionic charge and similar ionic radii, and should prefer the same coordination numbers, geometries and ligand types in their coordination complexes.

Various problems may arise during attempts to persuade microorganisms to accept a replacement metal. Such metal ions may give insoluble products with anions present in the growth medium or in the cell itself. Replacement metals, if taken up by the cell, may still fail to function as effective substitutes for native cations and give partially or completely inactive systems. This may result from incompatible redox properties, or more generally, because the replacement cation binds to the additional sites causing inhibition. The later situation commonly holds for the toxic cations. The replacement metal ion is inhibitory because it is insufficiently labile.

5.8 Effect of Various Physicochemical Factors on the Availability of Metals to Organisms

Several workers have performed several independent tests on different organisms and with different metals in order to find the individual effect of that particular metal on the test organism. Some studies have also been done on some fresh water organisms in the presence of many metals. The most commonly studied parameters are variation in temperature, dissolved oxygen (DO), pH, hardness, alkalinity and organic ligands.

The mechanisms whereby trace metal toxicity increases with higher temperatures can be explained by elevated respiratory activity (Lloyd, 1965). Thus rainbow trout in a zinc sulphate solution survived 2.35 times longer when the temperature was lowered from 22°C to 12°C. The temperature variation in Ganga and Yamuna waters between summer and winter is 20-22°C to 10-15 °C respectively.

Several researchers [e.g. Mancy and Allen, (1976)] have investigated the effect of change in pH on toxicity of the metals and have concluded that toxicity decreases with increasing pH because at high pH formation of metal oxide is favored. Ferris (1989) reported that at pH 8, microbial bioflims concentrate metals up to 12 orders of magnitude higher than that observed under acidic conditions. The four rivers studied have pH 8.0 ± 2. Hence, a similar effect with equal impact in all the four rivers is expected.

The reduction in metal toxicity by increased water hardness is well studied (Lloyd 1965; Herbert and Wakeford, 1962; Sprague, 1964). The degree of water hardness influences the toxicity and consequently the activity of trace metals by forming insoluble carbonates or by adsorption on calcium carbonate. Thus in hard waters, the concentration of trace metals necessary to reach the level of lethal dosage must be greater and lower when the hardness is less. Knowledge concerning the complexation and adsorption of trace metals with components of their aqueous environment is somewhat obscure because of the uncertainty associated with the role of hardness metal ions; specifically, calcium and magnesium, on these interactions. The presence of these metal ions in the natural environment at concentrations a thousand fold or more greater than that of the trace metals introduces the possibility that the coordination tendency of available ligands might be satisfied by the

hardness metal ions even though they generally form weaker complexes than the trace metals (Stumm and Morgan, 1981). The hardness causing metal ions would successfully compete with trace metals for available binding sites. The net result is an inhibition of trace metal complexation and/or adsorption, and a higher percentage of "free", hydrated metal in the aqueous phase. Such competitive interactions would certainly affect the distribution and dynamics of the trace metals and significantly alter their availability to aquatic organisms.

The chronic and acute criteria for the metals recognize that fresh water aquatic organisms would not be adversely affected if the 4 day average concentrations in μg/L of metal does not exceed the chronic level more than once every 3 years on the average (LaGerga *et al.*, 1994). Similarly there would be no adverse effect on the fresh water aquatic organisms if the 1 h average concentration does not exceed the acute values more than once in every 3 years on the average. A comparison of the acute and chronic levels of trace metals for organisms which inhabit the sediments with estimated range of trace metal concentration is presented in Table 5.2.

The data presented in Table 5.2 reveal that the Ganga water has values quite closer to the acute and the chronic criteria except for Cr and Ni. However, the concentration of Cr and Ni in the Ganga water is higher than that of the waters of other rivers. Hence, it shows that the Ganga water poses maximum constraints to aquatic microbes.

Table 5.2: Chronic and Acute Toxicity of Metals in the Four Rivers Studied

River	Metal	Acute Level (μg/L)	Chronic Level (μg/L)	Estimated Levels in the River (μg/L)	Number of Estimates
Ganga	Cd	2.00	0.76	3-11	12
Yamuna		3.50	1.00	1.4-3.0	4
Godavari		3.281	1.00	4.1-4.3	3
Narmada		5.781	1.48	1-2	3
Ganga	Cu	11.025	7.666	8-16	12
Yamuna		15.685	10.458	8-11.5	4
Godavari		15.271	10.329	4-5	3
Narmada		24.507	15.861	2-4	3
Ganga	Cr	1145.255	136.50	6.6-30.6	12
Yamuna		1536.851	183.18	9.0-15.6	4
Godavari		1525.515	181.83	<0.02	3
Narmada		2301.204	274.29	<0.02	3
Ganga	Pb	43.615	1.69	165-210	12
Yamuna		74.002	2.88	155-198	4
Godavari		66.759	2.60	36.4-37	3
Narmada		126.518	4.929	170-175	3
Ganga	Ni	923.35	102.64	36-54	12
Yamuna		1254.61	139.47	33.6-37.20	4
Godavari		1240.612	137.91	0.4-0.7	3
Narmada		1896.992	210.88	<0.02	3
Ganga	Zn	76.139	68.96	75-156	12
Yamuna		103.518	93.76	65-72	4
Godavari		102.343	92.69	25-27.5	3
Narmada		156.594	141.83	21-27.5	3

Miller and Mackay (1980) studied the effects of various combinations of alkalinity and hardness on LC_{50} values for rainbow trout. At a hardness of 12 mg/L, increasing the

alkalinity from 10-51 mg/L had no effect on the LC_{50} values. While at an alkalinity of 10 mg/L, increasing the hardness from 12 –100 mg/L increases the LC_{50} value by 3 fold. At hardness of 100 mg/L increasing the alkalinity significantly reduced Cu toxicity. Hardness and alkalinity of Ganga and Yamuna waters lie with in the aforementioned experimental range (Figure 5.8). Thus a similar effect with equal impact is expected in both Ganga and Yamuna waters. However, Godavari and Narmada waters are more alkaline than the Himalayan Rivers. Narmada water has the highest hardness of all the four rivers studied. Thus, more alkaline water means more availability of anion and consequently more complex formations and in turn higher LC_{50} values. The LC_{50} values for Ganga and Narmada waters are expected to be low and high respectively. Thus metals are less toxic at higher alkalinities that accompany higher hardness values. This may be due to the reduced bioavailability because of formation of metal (carbonate, hydroxy) complexes. Additionally, the availability of essential metals for microbial growth in Ganga water is much lower (Figure 5.9).

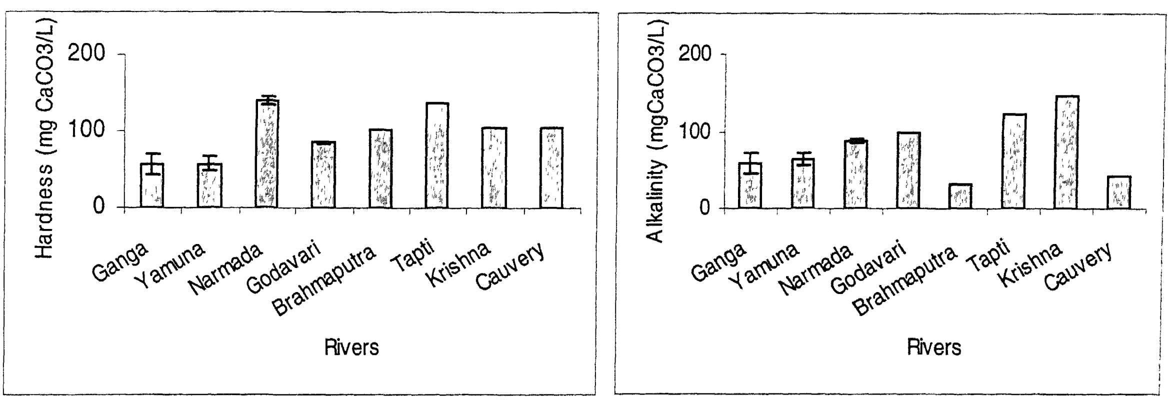

Figure 5.7: Mean and Range of Hardness and Alkalinity in Different Rivers of India. (Data for Rivers Brahamaputra and Tapti Reported by Subramanian, (1983); Data for the River Cauvery Reported by Subramanaian, (1985 b); Data for Krishna River reported by Ramesh, (1985); and the Remaining Data Obtained in the Present Study

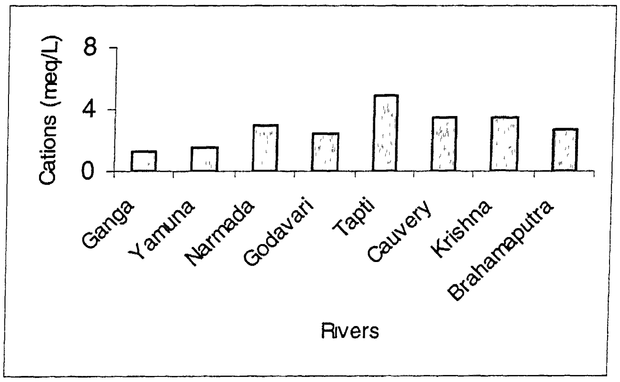

Figure 5.8: Essential Metal Contents Expressed as Total Cations in Different Rivers of India. (Data for Rivers Brahamaputra and Tapti Reported by Subramanian, (1983); Data for the River Cauvery Reported by Subramanaian, (1985 b); Data for Krishna River Reported by Ramesh, (1985); and the Remaining Data Obtained in the Present Study)

the acute toxicity of metals; apparently none that have evaluated effects on chronic toxicity. Winner (1985) studied the toxicity of Cu on *Daphnia Pulex* and *D. magna* to evaluate the interactive effect of humic acid (HA) and water hardness on the acute and chronic toxicity, and bioaccumulation of copper. In the absence of humic acid an increase in water hardness from 58 to 115 mg/L had no significant effect on the LC_{50} for copper. In the hard water (230 mg/L) the LC_{50} was significantly higher than in medium water. Humic acid (HA) significantly reduced the acute toxicity of copper; for each of the three water hardness, the LC_{50} was significantly higher in water containing 1.5 mg HA/L than in the same water to which no humic acid had been added. The reduction in copper bioaccumulation associated with a hardness increase from 58 to 115 mg/L can be interpreted as a result of an increased competition of calcium and copper for binding sites at biosurfaces. Thus hardness ions reduce toxicity of metals to aquatic life by competing with trace metals for binding sites. Alkalinity affects metal speciation directly by introducing the carbonate ligand and indirectly altering the pH of the medium.

Usually a number of chemical species are present in any water bodies. Thus aquatic organisms are being affected by mixtures of toxic substances of different origin. Some work has been done on the combined effect of metals on aquatic life. Enserink (1991) conducted experiments with *Daphnia magna*. Exposed to different mixtures of transition metals (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn), the LC_{50} limits were calculated to be 1.8

(0.89-3.1 TU) [TU (toxicity unit) is sum of the ratios of metals concentration to that of the LC $_{50}$ value]. Similar such experiment was done by Kay (1991) on filamentous bacteria in a system with calcium, copper, nickel, and zinc. All organisms grew best at the upper ranges of calcium concentrations. Trace metals are less toxic at higher level of calcium concentrations. Copper was more inhibitory than either nickel or zinc and copper-nickel and copper-zinc mixtures appeared to act synergistically in suppressing the development of bacteria. In contrast, nickel toxicity was reduced by the addition of zinc in the medium.

Based on the scale given by Enserink (1991) to convert Σ metals to TU, the toxicity units for the water of four rivers studied are presented in Table 5.3. The only limitation in adopting the conversion scale reported by Enserink (1991) is non availability of data on As and Hg concentrations in water of the various rivers considered in present study. The results show that the Ganga water has the highest TU.

Table 5.3: Estimated TU for the Waters of the Four Rivers

Rivers	TU	Range
Ganga	0.470	0.38-0.64
Yamuna	0.401	0.35-0.44
Godavari	0.265	(0.25-0.27)
Narmada	0.099	(0.09-0.10)

5.9 Effect of Alpha Radiation on Aquatic Organisms

In natural system radioisotopes are present in water in dissolved form, bed sediments, and in rocks. These isotopes emit radiations. Absorption of energy, released by the charged particles on passage through the cell, results in excitation or ionization of atoms. Such unstable atom reacts with nearby molecules in a very short time resulting in breakage of chemical bonds or oxidation of the affected molecules. The major effect in cells is DNA break. Microorganisms depend entirely on diffusion for their nutrition and removal of their waste product. Dissolved metals and radioisotopes enter into the cell through diffusion and slowly and slowly damage the cell. Lowe *et al.* (1956) have experimentally exhibited

bactericidal properties of irradiation. Although the acute and chronic levels are much higher than the levels estimated in the water samples of the four rivers, levels for the Ganga water are generally higher (Table 5.4).

Table 5.4: Chronic and Acute Toxicity of Uranium in Four Rivers

Rivers	Acute (Bq/L)	Chronic (Bq/L)	In Rivers (Bq/L)
Ganga	25520.639	16203.864	(4-100) $\times 10^{-3}$
Yamuna	50414.307	25041.605	(32-44) $\times 10^{-3}$
Narmada	57510.3367	40999.25	(6-16) $\times 10^{-3}$
Godavari	37160.045	23574.98	(9-13) $\times 10^{-3}$

5.10 Impact of River Water Quality on Microbial Growth

A 10 point scale for assessing the impact of individual metals for each of the four rivers has been formulated. The rating on the chosen scale was done based on the concentration of metals in water and the maximum inhibitory concentrations (MIC). The MIC was adopted from the studies conducted by different workers on different microorganisms. For each of the metals the rating is assigned 10 units if the concentration exceeds the MIC. Cumulative effect of the metals on the organisms present in the system is considered to be additive. Table 5.5 reveals that the concentration of Pb and Zn in Ganga water are disquieting for microbial growth.

Table 5.5: Impact Scores on 10 Point Scale for Different Metals in the Four Rivers Studied

Metal	MIC (μg/L)	Rivers	Metal Concentrations in River Waters (μg/L)	Assigned Impact Score
Cu	4-16	Ganga	13.769 ± 0.59	7.5-8.5
		Yamuna	9.015 ± 2.82	0-6
		Narmada	3.3 ± 0.855	0
		Godavari	4.485± 0.495	0
Cd	0.4-8.8	Ganga	5.515 ± 2.685	4-9
		Yamuna	2.375 ± 0.7	3-4
		Narmada	1.37 ± 0.455	0-3
		Godavari	4.132 ± 0.017	5
Ni	82-380	Ganga	39.303± 9.85	0
		Yamuna	34.5 ± 3.3	0
		Narmada	<0.02	0
		Godavari	0.6169 ± 0.14	0
Zn	0.047-120	Ganga	121.98 ± 31.52.	7.5->10
		Yamuna	69.78 ± 3.87	4.5-5.5
		Narmada	25.32 ± 0.155	1-1.5
		Godavari	26.64 ± 0.99	1-1.5
Pb	40-198	Ganga	188.7 ± 18.5	9->10
		Yamuna	180.75 ± 21	8->10
		Narmada	172.48 ± 2.007	8.5-9
		Godavari	36.653 ± 0.255	1.5-2
Cr	10-35	Ganga	11.34 ± 4.5	3-5
		Yamuna	12.45 ± 3.3	3-5
		Narmada	1.84 ± 0.43	0
		Godavari	3.745 ± 0.407	4

Winner (1985) studied the effect of humic acid and water hardness on the chronic no-observed effect concentration (NOEC) of copper for *Daphnia pulex.* Based on this study the multiplicative effect of trace metals, hardness and dissolved organic carbon on organisms was compared in the four rivers.

An increase in hardness from 58 to 115 mg $CaCO_3$/L with no humic acid, the LC_{50} value changes from 26 to 28 μg Cu/L i.e. 2 times increase in hardness results in 1 unit increase in LC_{50} value. For conservative estimates, the factor is taken to be 1.5 times rather than 2 times for 1 unit increase in LC_{50} value. A similar study by Winner (1985) for organic substances, showed that doubling the humic acid concentration (in the range 0 to 1.50 mg/L) at hardness of 58, 115, and 230 $CaCO_3$ mg/L leads to an increase in LC_{50} μg Cu/L value by 1.5 units. Again for conservative estimates, it is assumed that doubling the

concentration results in two fold increase in LC_{50} value. The logic behind this consideration is that an increase in humic acid concentration at a particular hardness results an increase in LC_{50} value. Similarly, an increase in hardness results in increase in LC_{50} value. Assuming that the effect of all the metals with change in water hardness and organic substance is similar, an overall impact score for apprehending microbial growth may be computed as follows.

Overall Impact Score = (Σ Individual Metal Impact Score)
x Impact Scaling Factor for Water Hardness
x Impact Scaling Factor for Organic Substances as measured by dissolved organic carbon

The overall impact factors for the waters of the four rivers studied are presented in Table 5.6. Results indicate that Ganga water poses restraints for microbial activity by several orders of magnitude higher than those of waters from other rivers.

Table 5.6: Comparative Assessment of Impact Score for Apprehending Microbial Activities in Rivers Ganga, Yamuna, Narmada and Godavari

Rivers	Σ Individual Metal Impact Score*	Hardness (mg/L as $CaCO_3$)	Impact Scaling Factor for Water Hardness	Dissolved Organic Carbon (mg/L)	Impact Scaling Factor Organic Substances	Overall Impact Score
Ganga	40	57.406	1.638	1.10	3.18	208.35
Yamuna	29	58.106	1.618	2.43	1.44	67.57
Narmada	13.25	141.04	0.667	3.5	1.0	8.84
Godavari	12.25	85.372	1.652	3.36	1.04	21.046

*As assigned in Table 5.5

6. Epilogue

The genesis of the present research was the belief since ages and the observations made through some studies that the Ganga water has some unique composition to maintain quality on prolonged storage. However, lack of sufficient evidences counteracts any special consideration while planning and executing major projects on or related to the river to preserve unique quality of the Ganga Waters. Therefore, this research was directed to address the issue of "Keeping quality" of Ganga water. It was contended that the Keeping quality would depend on the ability to arrest microbial activity which is generally responsible for deterioration in water quality on prolonged storage. It was postulated that the sustenance of microbial activities is governed by physicochemical characteristics of the water which in tern is influenced by rock/sediment water interactions. Efforts were made to gather scientific information for critically assessing the distinguishing features of the Ganga water that could be attributed to its unique composition. Some specific aspects of the physicochemical characteristics of water in the virgin stretches of the river Ganga were examined and compared with those of the other three important Indian rivers. The river stretches in the vicinity of their origins were selected to circumvent the influence of anthropogenic activities. Compare assessment of the potential of the river waters to apprehend microbial activities has been done. Based on the results of the present studies and synthesis of the available information, following conclusions may be drawn.

- Among the major rivers of ndia, bed sediments of Tapti are highly enriched in almost all the transition metals studied. Among the four rivers considered in the present study, Ganga bed sediments are impoverished in almost all the trace metals except lead. However, the concentration of trace metals in Ganga water is interestingly higher compared to the other rivers.

- Medium sized grains of Ganga sediments, as compared to coarse grains of Yamuna sediments and fine grains of Godavari and Narmada sediments appear to have played a significant role in higher trace metal content in the Ganga waters compared to waters of other rivers studied. Fine sediments in suspension seem to entrap and co-precipitate dissolved metals where as coarse-pebble sized grains

remain longer at one place and get longer time for the development of the oxy-hydroxide film that adsorbs the trace metals.

- Ganga and Yamuna waters contain low dissolved organics compared to Narmada and Godavari. Thus, chances of the formation of organo-metalic complexes in Ganga and Yamuna waters are less which help in apprehending microbial activities.

- Hardness of Ganga and Yamuna waters is typically lower than that of other Indian rivers. The low hardness increases the effectiveness of trace metals in arresting microbial activities.

- The thorium concentration in Ganga sediments is much higher in comparison to the other rivers while the uranium concentration in all the rivers is almost the same. The isotopes of uranium in Ganga water are comparatively much higher than that of the other rivers. The radioactivity is also higher in Ganga water.

- Overall, the Ganga water appears to have significantly higher potential to arrest microbial activity compared to the waters of the other rivers. This may be the plausible reason for the unique "keeping quality" of Ganga water.

Further studies should be conducted (i) to generate more information on the concentration of trace metals and radioactive elements in the river waters to permit statistical analysis, and (ii) to assess the relative potential of river waters for apprehending microbial activities.

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